

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)



16/50147

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Applicant's or agent's file reference ACD 2924 WO	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP03/01121	International filing date (day/month/year) 05.02.2003	Priority date (day/month/year) 22.02.2002
International Patent Classification (IPC) or both national classification and IPC C07C409/22		
Applicant AKZO NOBEL N.V. et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 3 sheets.

- This report contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  12.05.2003	Date of completion of this report  11.12.2003
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Heibl, C  Telephone No. +49 89 2399-8331  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP03/01121**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-17 as originally filed

**Claims, Numbers**

1-8 received on 22.08.2003 with letter of 21.08.2003

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP03/01121**

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-8
	No: Claims	
Inventive step (IS)	Yes: Claims	1-8
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-8
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP03/01121

**Re Item V-----**

(The numbering of the prior art documents (D1,D2..) cited hereinafter corresponds to the order in which they are mentioned in the International Search Report.)

The underlying object of the present invention was to provide 'Type 4' ketone peroxide compositions (and ester/carbonate derivatives thereof) which are sufficiently soluble in apolar hydrocarbon solvents and, thus, may advantageously be used in polymerization reactions where an apolar solvent is a prerequisite (e.g. in low-density polyethylene polymerisation (LDPE), production of PVC etc.).

Accordingly, the invention relates to compositions comprising

- a) a ketone peroxide  $\text{HOO-C(R}^1\text{)(R}^2\text{)-OOH}$  (or an ester/carbonate derivatives thereof) wherein  $\text{R}^1$  is a  $\text{C}_{1-4}$  alkyl or  $\text{C}_{2-4}$  alkenyl group and  $\text{R}^2$  is a  $\text{C}_{5-12}$  alkyl or alkenyl group and
- b) a branched or unbranched **hydrocarbon solvent** wherein the peroxide has a **solubility of at least 40 g/100g solvent at 20°C**, and which composition comprises **less than 10 wt%** of  $\text{H(OO-C(R}^1\text{)(R}^2\text{))}_2\text{-OO-H}$  (and the corresponding ester/carbonate derivatives thereof).

None of the prior art documents cited in the ISR discloses such compositions as defined above nor are such compositions directly and unambiguously derivable from any of these prior art documents. Consequently, the subject-matter of claims 1-6 may be considered as novel (Art. 33(2) PCT). The same applies with respect to the process for preparing the compositions of claims 1-6 (see claim 7) and their use as set out in present claim 8.

Although, D1, D2, D3 and D5 also relate to or inter alia include the provision of 'Type 4' ketone peroxide(s) (derivatives) and their use in polymerisation reactions, none of these documents teaches or suggests that by selecting a  $\text{C}_{5-12}$  alkyl or alkenyl group as substituent  $\text{R}^2$  (in particular, amyl or iso-amyl) a significant increase in solubility in apolar hydrocarbon solvents can be achieved, thereby allowing direct use of such peroxide compositions in polymerisation industry with improved results (Example 8). Reference is made in this respect to the findings set out in Table I of the present description.

The technical teaching of D4, D6 and D7 are considered to be still more remote as they

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP03/01121

are concerned with objects which are quite different from that underlying the present invention (D4: reduction of explosiveness of organic peroxides in general; D6: safe handling of aldehyde or ketone peroxides; D7: provision of compositions containing a halogenated ketone peroxide and one or more inert organic solvents). These documents do not describe or suggest a specific ('Type 4') ketone peroxide compositions sufficiently soluble (at least 40g/100g) in hydro carbon solvents and having less than 10 wt% of the undesired peroxide products as indicated in the present claims.

Having regard to the present state of the art, the subject-matter of claims 1-8 is also considered to meet the requirements of Art. 33(3) PCT.

The criterion of Art. 33(4) PCT (industrial applicability) is also met.

## CLAIMS

92

1. A composition of a ketone peroxide comprising
  - a) a peroxide derivative of the formula  
 $\text{HOO-C(R}_1\text{)(R}_2\text{)-OOH}$   
wherein  
 $\text{R}_1$  is a branched or unbranched alkyl group with 1 to 4 carbon atoms or alkenyl group with 2 to 4 carbon atoms; and  
 $\text{R}_2$  is a branched or unbranched alkyl or alkenyl group with 5 to 12 carbon atoms; and
  - b) a branched or unbranched hydrocarbon solvent;  
the peroxide derivative of a) having a solubility more than 40 g in 100 g of the solvent of b) at 20°C; and  
comprises less than 10 wt.% of a peroxide derivative of the formula  
 $\text{HOO-C(R}_1\text{)(R}_2\text{)-OO-C(R}_1\text{)(R}_2\text{)-OOH}$ ,  
wherein  $\text{R}_1$  and  $\text{R}_2$  have the previously given meanings.
2. The composition of claim 1 wherein  $\text{R}_1$  and  $\text{R}_2$  are alkyl groups.
3. The composition of claim 2 wherein  $\text{R}_1$  is a methyl group and  $\text{R}_2$  is an isoamyl or amyl group.
4. The composition of any one of claims 1-3 wherein the solvent is a saturated aliphatic hydrocarbon.
5. A composition of a ketone peroxide derived bis-peroxyester, bis-peroxycarbonate, or mixed peroxyester-peroxycarbonate comprising
  - a) a ketone peroxide derived bis-peroxyester, bis-peroxycarbonate, or mixed peroxyester-peroxycarbonate derivative of the formula  
 $\text{R}_3[\text{O}]_n\text{C(O)OO-C(R}_1\text{)(R}_2\text{)-OOC(O)[O]}_n\text{R}_3$   
wherein  
 $\text{R}_1$  is a branched or unbranched alkyl group with 1 to 4 carbon atoms or alkenyl group with 2 to 4 carbon atoms; and  
 $\text{R}_2$  is a branched or unbranched alkyl or alkenyl group with 5 to 12

carbon atoms; and

$R_3$  is independently selected from a branched or unbranched alkyl group with 1 to 12 carbon atoms, alkenyl group with 2 to 12 carbon atoms; and an aromatic group with 6-12 carbon atoms,

$n$  is independently 0 or 1, and

- b) a branched or unbranched hydrocarbon solvent;

and

comprising less than 10 wt.% of a peroxide derivative of the formula

$R_3[O]_nC(O)OO-C(R_1)(R_2)-OO-C(R_1)(R_2)-OOC(O)[O]_nR_3$ ,

wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $n$  have the previously given meanings.

6. A composition of a ketone peroxide derived monoperoxyester or monoperoxycarbonate comprising

- a) a ketone peroxide derived monoperoxyester or monoperoxycarbonate derivative of the formula

$HOO-C(R_1)(R_2)-OOC(O)[O]_nR_3$

wherein

$R_1$  is a branched or unbranched alkyl group with 1 to 4 carbon atoms or alkenyl group with 2 to 4 carbon atoms; and

$R_2$  is a branched or unbranched alkyl or alkenyl group with 5 to 12 carbon atoms; and

$R_3$  is selected from a branched or unbranched alkyl group with 1 to 12 carbon atoms, alkenyl with 2 to 12 carbon atoms; and an aromatic group with 6-12 carbon atoms;

$n$  is 0 or 1, and

- b) a branched or unbranched hydrocarbon solvent;

and

comprising less than 10 wt.% of a peroxide derivative of the formula

$HOO-C(R_1)(R_2)-OO-C(R_1)(R_2)-OOC(O)[O]_nR_3$ ,

wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $n$  have the previously given meanings.

7. A process for the preparation of a composition of any one of the claims 1-4 comprising the step wherein a ketone of the formula  $O=C(R_1)(R_2)$ , wherein  $R_1$  and  $R_2$  have the previously given meanings, is reacted with hydrogen peroxide

in the branched or unbranched hydrocarbon solvent in the presence of an acidic catalyst.

8. Use of the composition of any one of claims 1-6 for polymerizing vinylchloride, (meth)acrylic monomers, styrene, ethylene, or mixtures thereof, for curing unsaturated polyester or vinylester resins, for grafting monomers onto a polymer, for crosslinking a polymer or for degrading a polymer.